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**NON-GASSING NICKEL-CADMIUM BATTERY ELECTRODES AND CELLS –
TESTING OF 25 Ah CELLS**

Report No. 712-122-5

**Supplementary Report
25 August 1972 to 25 November 1972**

Prepared by E. Luksha and D.J. Gordy

Approved by C.J. Menard

23 February 1973

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**Jet Propulsion Laboratory
Contract No. 953184**

**Gould Inc., Gould Laboratories
Energy Technology
1110 Highway 110
Mendota Heights, Minnesota 55118**

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I. SUMMARY

There are various special applications for very long-lived, a decade or more, sealed nickel-cadmium batteries. The gassing which normally occurs in such cells limits their lives severely and in many cases is the sole cause of failure. An approach toward dramatically increasing their lives is to incorporate electrodes in these batteries that exhibit little or no gassing with controlled charge input.

This requires: 1) the ratio of positive active material be changed to make cells negative limited, and 2) use materials that possess the highest possible over-potentials for the hydrogen evolution reaction so that the onset of hydrogen gassing would result in a large voltage step to be used to cut off the charge.

This report describes the testing of 30 practical size, experimental 25 Ah cells constructed as part of an earlier negative limited cell development program. The test results showed that the negative limited cell is a possible means of developing a long-lived secondary cell.

The cells were tested for 500 cycles using an accelerated regime approximating a 90-minute orbit period. Three groups of ten cells each were tested at 0°, 25°, and 40°C. The cycle data showed that the negative limited cells had higher degradation rates at the higher operating temperatures. At the conclusion of 500 cycles, the three groups had average capacities of 16.83, 12.74, and 5.71 Ah for testing at 0°, 25°, 40°C, respectively. The conditioning capacities of these cells was in the 25 Ah range.

The internal cell pressures of the three groups was also temperature dependent and was, in general, in the 2 psig range during the course of the test program. No periodic variation of the internal pressure with the state-of-charge was observed except with some cells tested at 40°C.

II. INTRODUCTION

There is presently a need for very reliable and very long-lived, about one decade, secondary batteries for applications such as deep probe space vehicles, medical implantations, various cordless appliances, and other special uses. Sealed nickel-cadmium batteries are uniquely suited for such applications, mainly because of their long lives. However, the gassing that normally occurs in these cells, limits their reliability for very long life. The gassing problem becomes particularly severe during latter states of the cell life. Aging effects on both electrodes can result in a set of circumstances that sealed cells can rupture due to hydrogen generation on charge. In many cases, gas evolution is the sole cause of life limitation of nickel-cadmium cells. As a result, an approach toward increasing the life of nickel-cadmium cells toward the decade or so required, is to construct cells designed with little or no gassing. The Jet Propulsion Laboratories have suggested an approach leading to the development of a 'non-gassing' nickel-cadmium battery. Their approach involves essentially three changes in the design of conventional nickel-cadmium batteries. These are:

1. Change the ratio of positive to negative active material in the cells so that the cells become negative limited
2. Use a grid material for the cadmium electrode that has a high over-potential for the hydrogen evolution reaction so that the onset of hydrogen gassing would be signaled by a relatively large voltage step
3. Incorporation of a miniature electronic charge control device that will be used externally to each cell to end the charge using the voltage step as a signal

Gould Inc., Energy Technology Laboratories, under subcontract to JPL is involved in the design, development, and testing of a 'non-gassing' battery in accordance with parts 1 and 2 above.

In an earlier report (Ref 1) on this subject, the work conducted at Gould Inc. toward these goals was described. The concept of a negative limited 'non-gassing' nickel-cadmium battery was demonstrated by constructing and testing practical size experimental cells of approximately 25 Ah capacity. Thirty cells were constructed for extensive testing. It is the testing of these cells that is the subject of this report.

III. EXPERIMENTAL

A. Cadmium Electrodes

Electrodes were prepared using a laboratory version of a proprietary production process whereby a cadmium active mass was deposited on a 5 Ag 7 - 4/0 expanded silver screen (Exmet Corp.). These electrodes were prepared in 17.0" x 5.0" dimensions and then cut to 4.75" x 3.25" sizes for use in the test cells. These electrodes were 0.014 - 0.016 inches thick and had average loadings of 0.91 g/in.²

B. Nickel Electrode Preparation

Inco 287 powder was used for the preparation of positive electrodes. The powder was first dried in a vacuum oven for one hour at 210°C. After removal from the oven, the powder was placed in a dry room to cool. When cool, the powder was placed in a set of standard sieves and processed on a Ro-Tap shaker for 15 minutes. The 1.04 g/cc (Scott Densiometer, the -37 μ fraction) fraction was stored in a dry room until used. A portion of the powder was sprinkled into a 6 x 12 inch mold containing a 20-mesh wire-woven nickel screen. The powder was removed from the mold and sintered in a vacuum furnace for 10 minutes at 1675°F. The plaques thusly prepared were first cut into 4.75 x 3.25 inch sizes, coined, and then current collector tabs were welded on. The thickness of the plaques was 51 mils.

Four-hundred twenty such plaques were impregnated using one of Gould's private processes, to a loading of 1.925 ± 0.056 g/cc.

C. Cell Construction

Thirty 25 Ah cells were fabricated, each containing 11 nickel electrodes and 10 cadmium electrodes of the 4.75 x 3.25 inch sizes. The separation employed was 10 mil Pellon 2504. The electrode packs were assembled in polypropylene oxide cell hardware supplied by JPL. The posts were silver plated copper onto which the electrode tabs were silver soldered. The cells were sealed with Allaco Products All-Bond epoxy resin. The target positive/negative active material ratio was 3:1.

After the cells were thusly assembled they were flooded with 30% mercury cell grade KOH and then charged at 2 amps for 16 hours. The cells expelled electrolyte during this conditioning charge, leaving 160 cc/cell. This charge was followed by a 3 amp discharge to 0.0 volt. The cells were again charged at 2 amps for 16 hours and the capacity was measured (called the conditioning capacity) using a 3 amp discharge to 0.0 volt. No additional electrolyte was expelled. The cells were again charged at 2 amps for 16 hours and at this point Trerice dual range compound pressure gauges were attached to the cells. The tubes and sockets of the gauges were fabricated from 316 stainless steel. A test cell is shown in Figure III-1. When a group of 10 cells was ready for testing, they were placed in a Tenny 5 environmental chamber at the appropriate temperature and allowed to equilibrate overnight.

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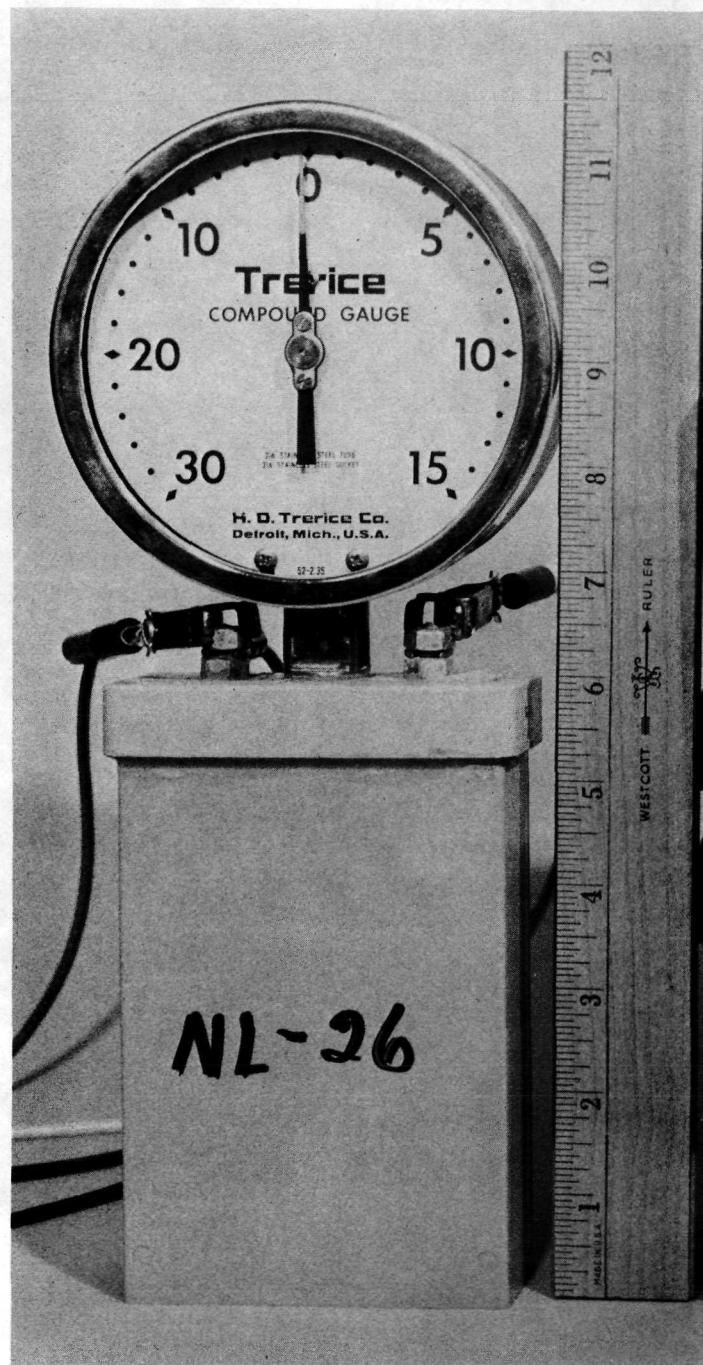


FIGURE III-1. TEST CELL

The void volume in the test cells was 35 cc, a value which was computed from the measured void volumes of the test cell components. The pressure gauges contributed 8 cc to this volume. The inside volume of the empty cell cases was 400 cc.

D. Test Program

Ten cells were tested each at 0°, 25°, and 40°C for 500 cycles or until failure. The cycling regime included the following procedures:

- Conditioning capacity measurement with a 2 amp charge for 16 hours, while the cells were still open, followed by a 3 amp discharge to 0.00 volt. The charge and discharge were performed at room temperature.
- Accelerated cycling which approximated a 90-minute orbit period, included a 12.5 amp charge to a 1.75 volt cutoff followed by a 14.5 amp discharge for 42 minutes or to a 0.0 volt cutoff. Only the group tested at 40°C reached the cutoff during the high-rate cycling.
- The capacities of these cells were measured approximately every 50 cycles using a 2 amp charge to 1.75 volts and a 3 amp discharge to 0.0 volt.
- Pressure measurements were taken at random (as far as the state-of-charge was concerned) twice daily during each working day.

IV. RESULTS AND DISCUSSION

A. Cell Testing At 0°C

The average capacities and the 95% confidence limits which are shown as error bars, of the 10 cells tested at 0°C are shown in Figure IV-1 at approximately 50 cycle intervals. These capacities were determined with a 2 amp charge to 1.75 volts and a 3 amp discharge to 0.0 volt. This group of cells had an average capacity of 25.15 ± 0.10 Ah measured during a conditioning cycle at room temperature. The first cycle capacity at 0°C was not measured, but would have been in the 22-23 Ah range. After 507 accelerated cycles, this group of cells had an average capacity of 16.83 ± 1.93 Ah, the larger part of the capacity degradation occurring within the first 200 cycles. After 500 cycles, the capacity was apparently increasing!

Within the accuracy of the test equipment, the input/output efficiency was observed to be 100%. The capacity degradation was therefore a result of a decrease in the available capacity of the cadmium electrode.

The average cell pressure, again of the 10 cells, is shown in Figure IV-2. The error bars indicate the 95% confidence limit for the given average. At the start of the cycle testing, the average internal cell pressure, at 0°C was in the -3psig range. The initial negative internal pressure was due to oxygen recombination in the cell during stand on open-circuit. The oxygen was introduced during the cell construction and conditioning which were performed while the cells were in the vented condition. The cell pressure increased gradually to the 1 psig range over the first 100 cycles where it remained for the balance of the 500 test cycles.

No periodic variation in the internal cell pressure that could be related to their state-of-charge was observed. However, the internal pressure of some cells did vary a few psig at different stages in the test program. On the other hand, other cells showed no variation during the entire test program.

This group of cells completed the test program without a cell failure.

B. Cell Testing At 25°C

The average capacities and the 95% confidence limits for the 10 cells tested at 25°C are given in Figure IV-3. The capacities were once again determined using a 2 amp charge to 1.75 volts and a 3 amp discharge to 0.0 volt approximately every 50 cycles. The cycles between the capacity measurement cycles were performed using the accelerated regime described above. The 25°C test group had an average capacity of 25.32 ± 1.85 Ah measured during a conditioning cycle at room temperature. Figure IV-3 shows the average cell capacity degrading at a rate of 0.13% per cycle for the first 400 cycles at which point the rate of degradation apparently changes and levels out. At the 500 cycle mark the average cell capacity, as with the group tested at 0°C, is increasing. At the conclusion of the testing, 503 cycles, the average cell capacity was 12.74 ± 2.83 Ah.

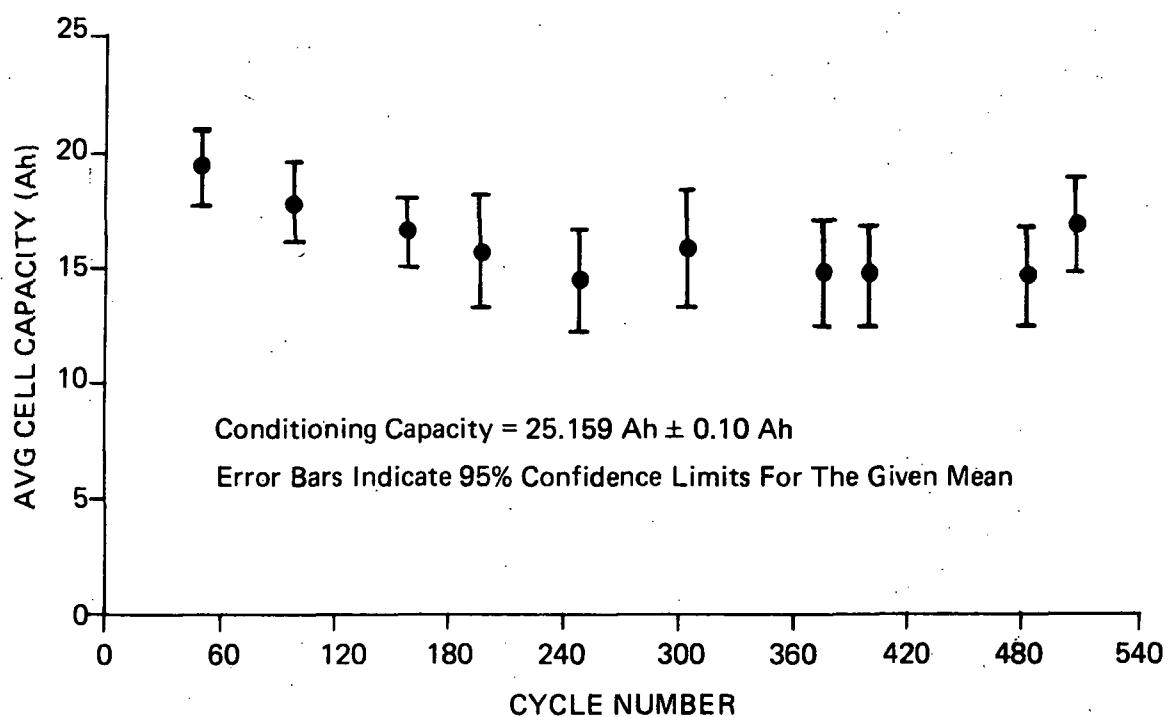


FIGURE IV-1. VARIATION OF AVERAGE CELL CAPACITY WITH CYCLE NUMBER AT 0°C

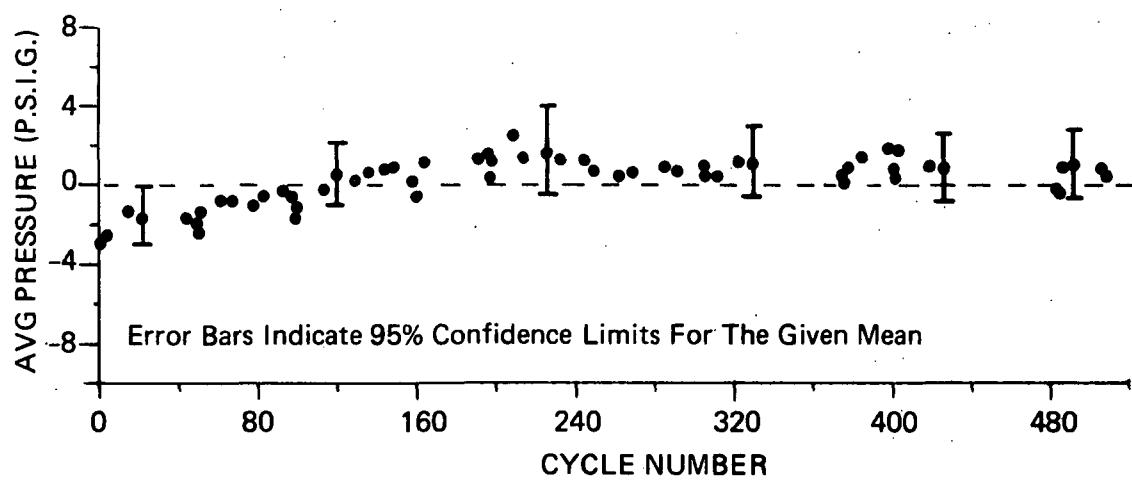


FIGURE IV-2. AVERAGE CELL PRESSURE AS A FUNCTION OF CYCLE NUMBER AT 0°C

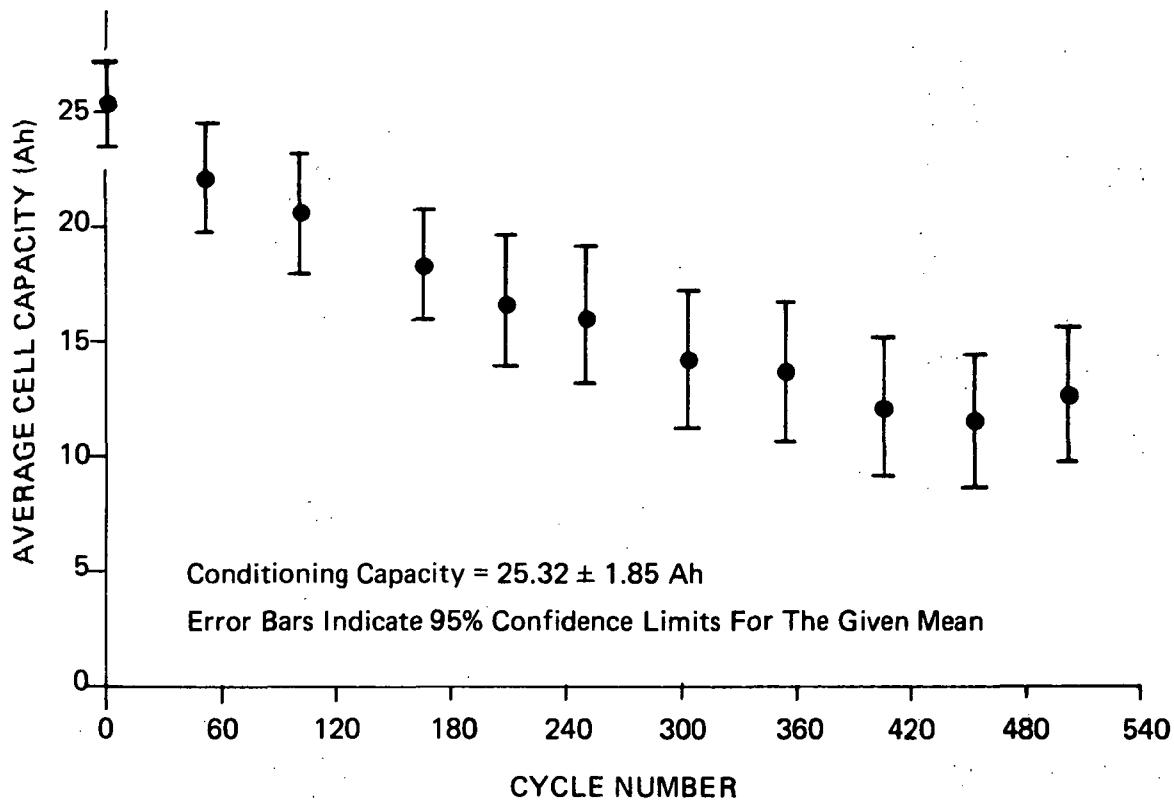


FIGURE IV-3. VARIATION OF AVERAGE CELL CAPACITY WITH CYCLE NUMBER AT 25°C

As was observed with the first group of test cells, the input/output efficiency for the test cycle was 100%, so that the degradation in capacity was due to a decrease in capacity of the cadmium electrode.

The average cell pressures as a function of cycle number for the 10 cells tested at 25°C are given in Figure IV-4. The error bars are the 95% confidence limits for the appropriate average. Unlike the first group, the initial internal cell pressure was in most cases several psig higher and positive in sign. Also, more variation in the experimental points is evident. However, there was no increase in pressure observed during the test program. The pressure remained at a 'smoothed' value of 2 psig (from Figure IV-4) for the duration of the test program.

As with the cells tested at 0°C, no periodic variation in the internal cell pressure of the individual cells was observed that could be correlated to the cell's state-of-charge. The internal pressure in the individual cells did vary several psig during the test program however.

All ten cells tested at 25°C completed the test program without failure.

C. Cell Testing At 40°C

Previous work indicated (Ref 1) that cell performance from the point of view of capacity degradation and gassing would be most severely tested at 40°C. This proved to be the case again. In addition, other inexplicable difficulties were encountered which added to the problems. The average cell capacities along with the 95% confidence limits are given in Figure IV-5. This group of cells had an average conditioning cycle capacity of 22.57 ± 1.14 Ah. This value is well below the 25 Ah value measured for the other two groups. We have no reasonable explanation for this result. The initial average capacity was 20.63 ± 1.06 Ah, also the lowest of the three groups. We expected a value higher than the one obtained since it was found that cadmium electrode efficiency improved with increasing charge temperature. The fact that the conditioning capacity and the first cycle capacity are well below the expected values of 25 and 28 Ah, respectively, suggests these were not of the quality they perhaps could be, due to 'bugs' introduced in their manufacture and storage. The capacity data given in Figure IV-5 shows a very large drop in capacity over the first 100 cycles, from 20.6 to 10.8 Ah, whereupon the capacity degrades at a far lower rate for the remainder of the 500 test cycles. At the conclusion of the cycle testing, the group average capacity was in the 6 Ah range.

The average cell pressures are shown in Figure IV-6. The initial pressures show considerable variation during the initial 100 cycles and absolute values higher than measured for the test groups tested at 0° and 25°C, these high values being a reflection of high pressures in a few cells. After 100 cycles, the pressures leveled out and remained at 2 psig for the remainder of the test program.

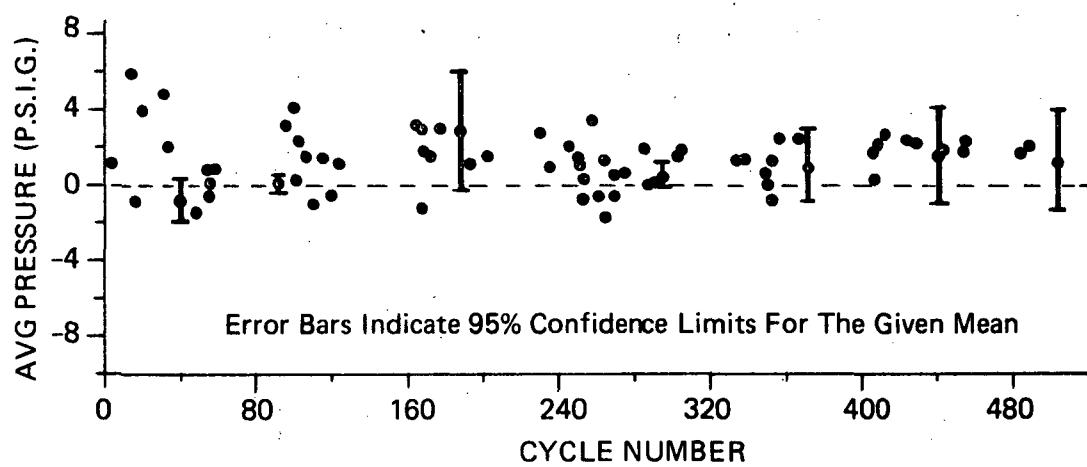


FIGURE IV-4. AVERAGE CELL PRESSURE AS A FUNCTION OF CYCLE NUMBER AT 25°C

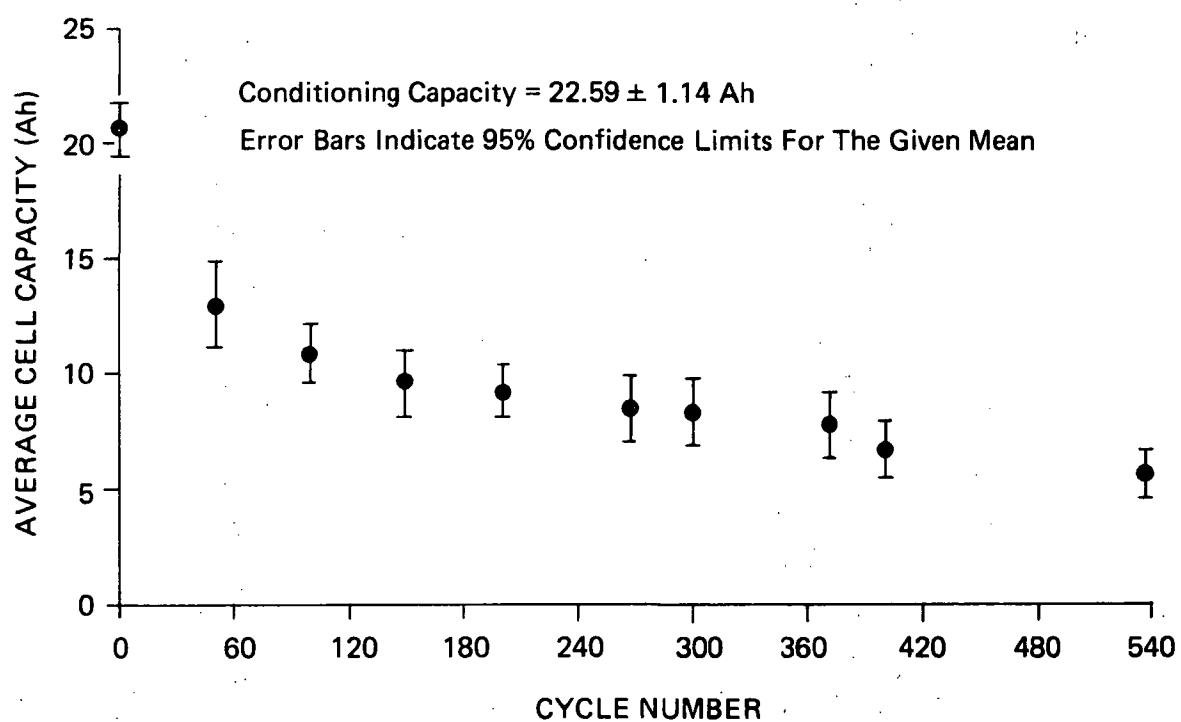


FIGURE IV-5. VARIATION OF AVERAGE CELL CAPACITY
WITH CYCLE NUMBER AT 40°C

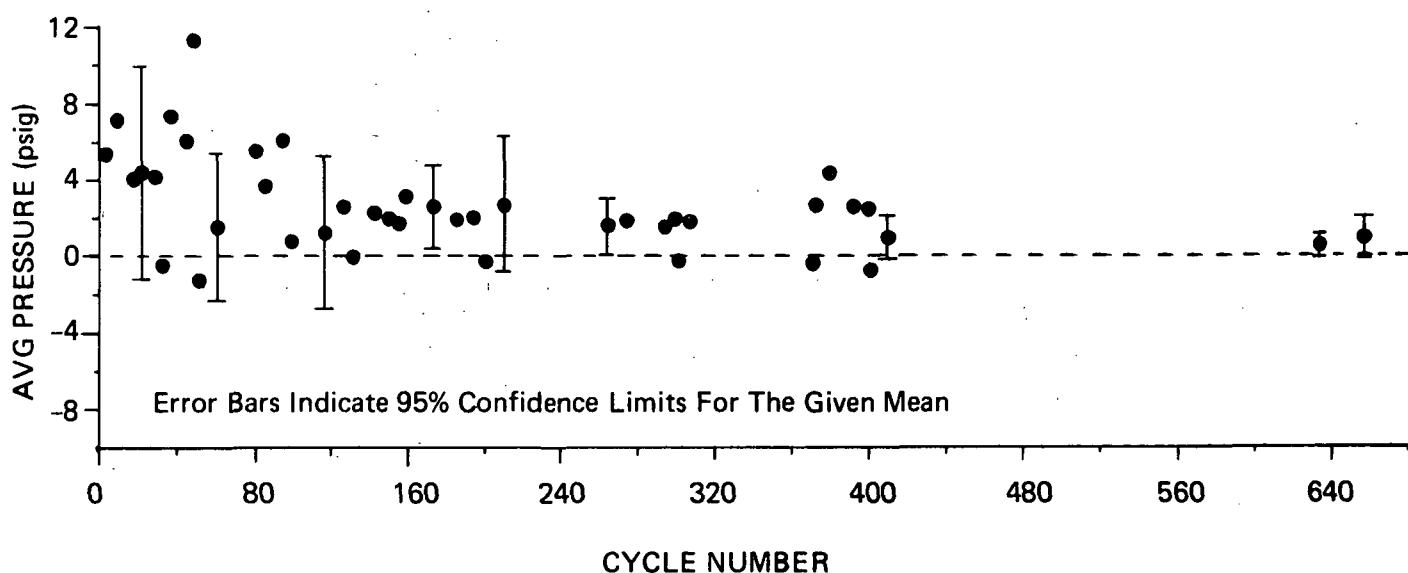


FIGURE IV-6. AVERAGE CELL PRESSURE AS A FUNCTION
OF CYCLE NUMBER AT 40°C

Unlike the other two test groups, the internal pressure of some cells did vary with the state-of-charge of the cell, the pressure increasing on charge and decreasing on discharge. Some cells showed no periodic variation of pressure that could be related to their state-of-charge.

Five cells in this group failed. One developed a leak in the terminal post, two others failed due to internal shorts, and two others failed due to leaks in the plastic hardware.

D. Cell Gassing

The test data strongly suggests that small quantities of oxygen are being evolved in the cells. Assuming negligible recombination at the charge/discharge rates employed, it is possible to estimate the evolution rate for a ΔP of 1 psig as follows:

$$i = \frac{4\Delta PVF}{(14.7)RTtA}$$

where:

P = 1 psig

V = 0.035 liters

F = 26.81 Ah

T = absolute temperature

R = 0.8205 liter - Atm/deg-mole

t = 0.7 hour (42 minute charge)

A = electrode area, 170 in.²

The current corresponding to oxygen evolution estimated in this way is 9.5×10^{-6} , 8.7×10^{-6} , and 8.3×10^{-6} amps/in.² for 0°, 25°, and 40°C. These values are well below the 1×10^{-4} amps/in.² limit of detection reported earlier (Ref 1).

E. Cell Voltage Characteristics

Figures IV-7, IV-8, and IV-9 show the average cell voltage for the charge and discharge on a capacity measurement cycle, at 0°, 25°, and 40°C, respectively. The cells were not fully discharged prior to the charges shown. The potential steps shown in Figures IV-7 through IV-9 were large enough and short enough to signal end-of-charge before hydrogen evolution for all the test conditions in this work.

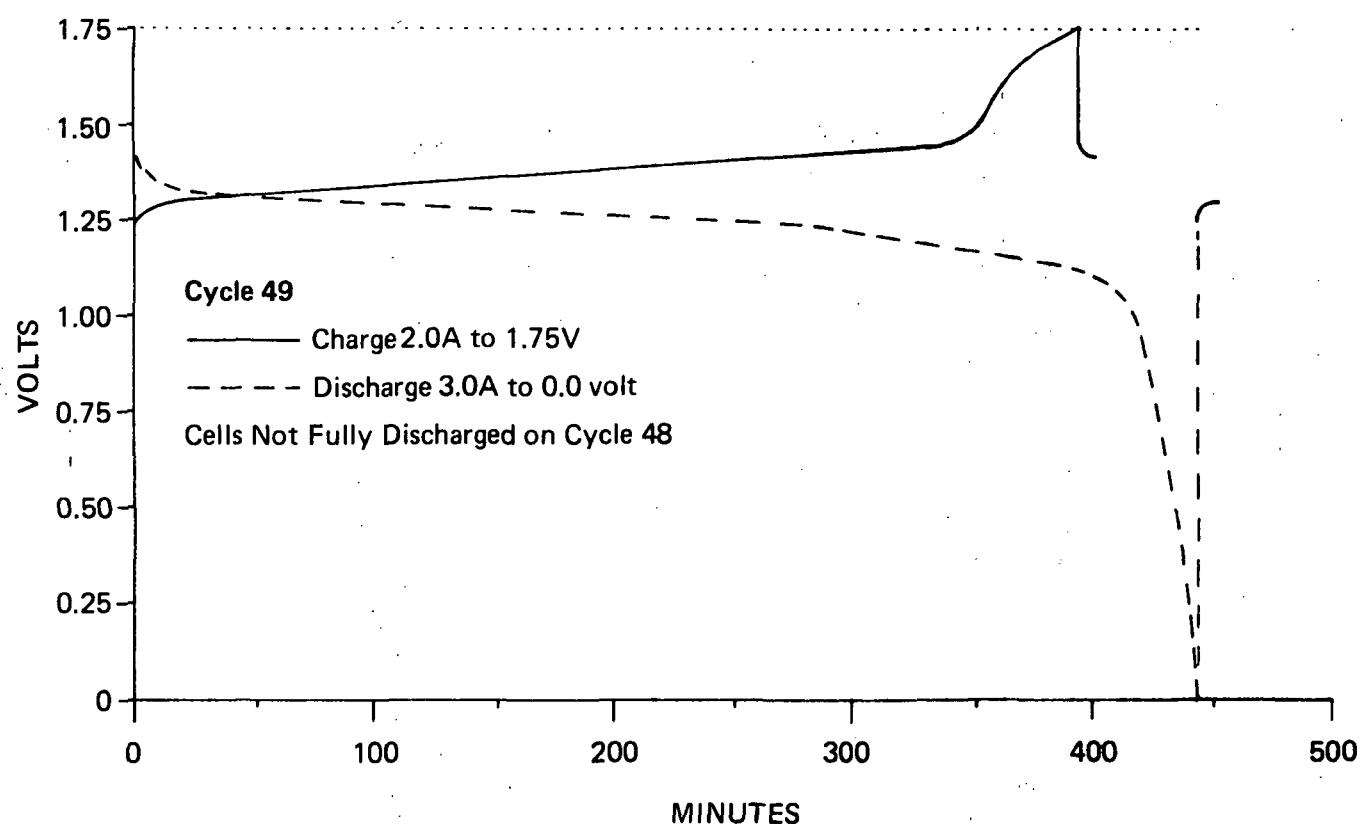
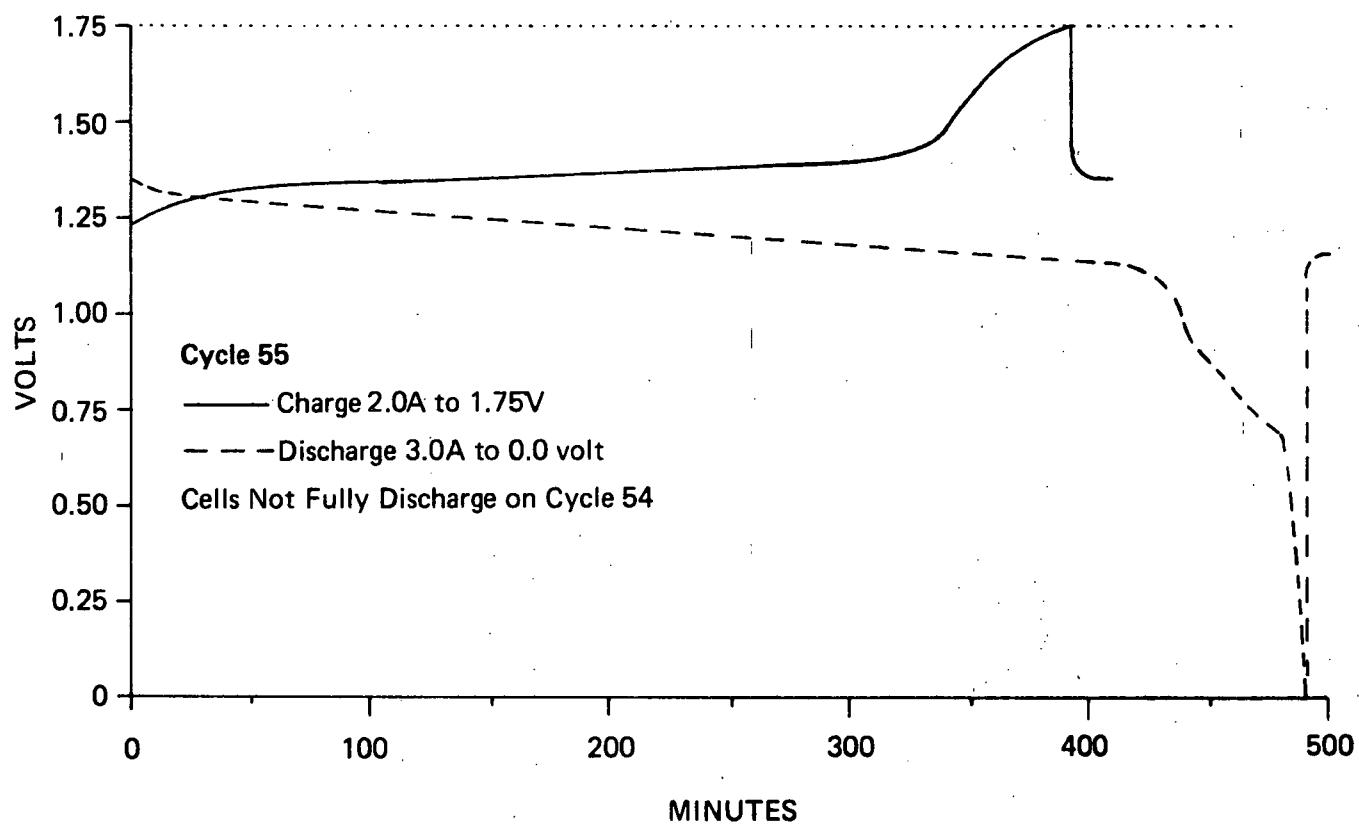


FIGURE IV-7. AVERAGE CELL VOLTAGES ON
CHARGE AND DISCHARGE AT 0°C



**FIGURE IV-8. AVERAGE CELL VOLTAGES ON
CHARGE AND DISCHARGE AT 25°C**

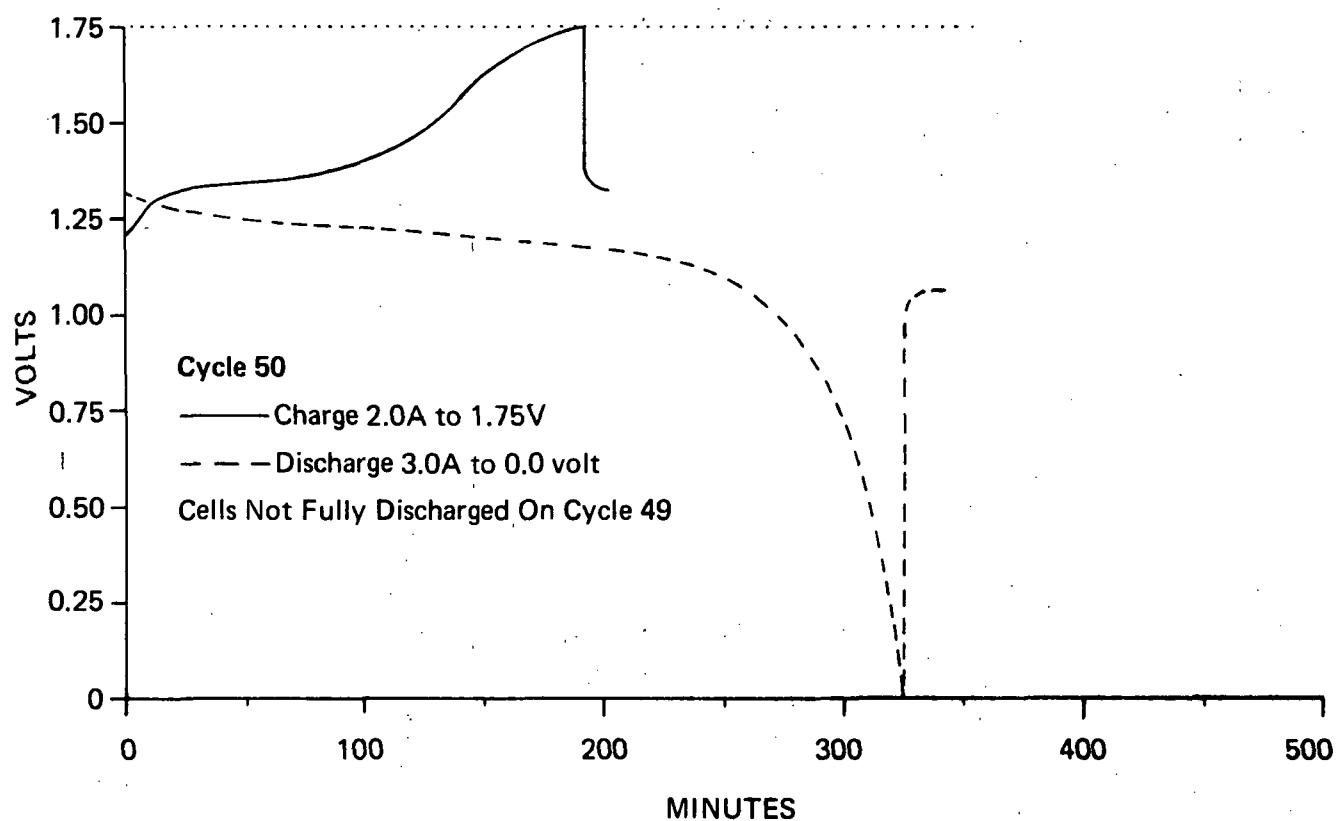


FIGURE IV-9. AVERAGE CELL VOLTAGES ON
CHARGE AND DISCHARGE AT 40°C

V. CONCLUSIONS

The negative limited 'non-gassing' cell with intrinsic charge control was shown to be a possible means of increasing the life of nickel-cadmium cells.

Thirty 25 Ah negative limited 'non-gassing' nickel-cadmium cells were tested for 500 cycles using an accelerated regime approximating a 90-minute orbit period (a charge of about 45 minutes to 1.75 volts, and a 45-minute discharge to 40% depth). Three groups of 10 cells each were tested at 0°, 25°, and 40°C.

In general, the cycle test data showed that the negative limited cells have higher ampere-hour degradation rates at higher operating temperatures. The group of cells tested at 0°C had initial capacities of 22 Ah (estimated) and at the end of 500 cycles had an average capacity of 16.83 Ah, a rather interestingly high value. The group of cells tested at 25°C had an average conditioning capacity of 25.32 Ah and after 500 cycles had an average capacity of 12.74 Ah. The cells tested at 40°C had a conditioning cycle capacity of 22.58 Ah. The capacity of this group degraded to 5.71 Ah after 535 cycles.

The internal cell pressures followed a similar trend in that cell pressures were higher at the higher operating temperatures. The cells tested at 0°C had a group average pressure of -3 psig initially which increased to 1 psig over the first 100 cycles where it remained for the duration of the test program. The cells tested at 25°C had a group average internal pressure of 2 psig.

The pressure remained at this value during the entire test regime. No periodic variation of internal cell pressure with state-of-charge was observed with either of these two groups of cells. Also, there were no failures in these two groups of cells. At 40°C the initial cell pressures were in the 4 psig range but leveled out at 2 psig after 100 cycles and remained at that level for the balance of the test program. Five cells in this group failed due to internal shorts or leaks in the hardware.

Thus, the negative limited nickel-cadmium cell is a promising avenue leading toward the development of a long-lived secondary cell. Its most outstanding limitation is its capacity degradation, especially at the higher operating temperatures.

VI. REFERENCES

1. E. Luksha, D.J. Gordy, and C.J. Menard, "Non-Gassing Nickel-Cadmium Battery Electrodes and Cells", Report No: 712-122-4. Prepared for Jet Propulsion Laboratory, Contract No. 953184.